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Co-Mediated Coupling

A. W. Thomas, S. V. Ley

Pd-Catalyzed Cross-Coupling

A. Zapf

Reduction Catalysts

W. R. Thiel

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H/D Exchange in an Excited Hydride

Excited-State Deprotonation and H/D Exchange of an Iridium Hydride Complex*

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Dedicated to Professor Fritz Wastgestan on the occasion of his 70th birthday

Excited-state proton transfer from hydroxyarenes has been known for long time^[1] and studied extensively.^[2–8] Simple thermodynamic considerations, for both the ground and excited states of any proton-containing molecule and its conjugate base, indicate that the excited state is a much stronger acid than the corresponding ground state.^[2–4] Extremely strong acids can be produced by photoexciting hydroxyaromatic compounds that carry electron withdrawing groups—commonly referred to as “super” photoacids.^[5–9] A widely accepted rationalization for the enhanced acidity in the excited state infers an intramolecular charge transfer (ICT)—in the excited state of the acid from the hydroxyl oxygen to the aromatic ring.^[10–14] In addition to hydroxyarene-type photoacids, so-called photoacid generators (PAG) exhibit promising activities.^[15] The performance of such PAGs is, however, limited to exposure of UV light ($\lambda < 400$ nm). A photoacid that operates under visible light illumination is desired when visible light lasers such as He–Cd, YAG, and Ar ion lasers are necessary as a high-power and stable light source for microlithographic and holographic applications.^[16]

In contrast to organic photoacids, metal hydride complexes, which also contain removable protons, have never been shown to act as photoacids. In particular, the hydride in metal hydride complexes is believed to be electronegative and, in turn, difficult to remove in the form of protons.

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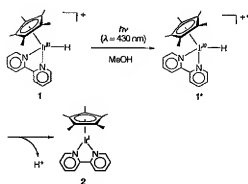


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However, the release of protons occurs in some metal hydride complexes as indicated by the H/D exchange reactions in water.^[11]

We wish to report herein the first example of: 1) excited state deprotonation in a hexafluorophosphate salt of an iridium hydride complex (**1**)^[12,13] which absorbs visible light ($\lambda_{\text{max}} = 430 \text{ nm}$); and 2) the H/D exchange reaction in the excited state.

No spectral changes of the absorption features are noted when a methanol solution of **1** was photoirradiated in the steady state with visible light ($\lambda > 400 \text{ nm}$) at room temperature. Transient absorption bands at $\lambda_{\text{max}} = 490, 530(\text{sh}), 620, 670$, and 730 nm are, on the other hand, observed upon nanosecond laser pulse excitation ($\lambda = 430 \text{ nm}$) as shown in Figure 1 a. These newly formed absorption bands are assigned



Scheme 1. Photoinduced deprotonation of **1** to form **2**.

mechanism was further confirmed by the change of deprotonation kinetics from second-order to pseudo-first-order in the presence of large excess trifluoroacetic acid (CF_3COOH). The pseudo-first-order rate constant linearly increases with increasing $[\text{CF}_3\text{COOH}]$ (see Supporting Information).

When we replaced CH_3OH with $[\text{D}_5]\text{methanol} (\text{CD}_3\text{OD})$, the decay rate of **2** became significantly slower (Figure 1 b). A large kinetic deuterium isotope effect ($k_{\text{H}}/k_{\text{D}} = 8.2$) is derived from the slopes of the second-order plots.^[13]

The formation of **1*** and the subsequent deprotonation process were successfully observed by picosecond laser flash photolysis as shown in Figure 2. Upon laser excitation ($\lambda =$

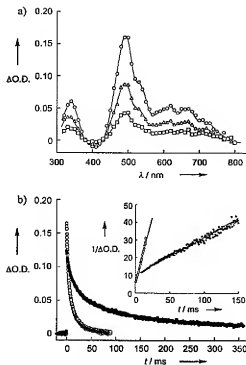


Figure 1. a) Transient absorption spectra observed in photoinduced deprotonation of **1** ($2.4 \times 10^{-4} \text{ M}$) at $10 \mu\text{s}$ (\circ), 4 ms (Δ), and 12 ms (\square) after laser excitation ($\lambda = 430 \text{ nm}$, 10 mJ/pulse) in deaerated CH_3OH ; b) time-course of the absorbance change at $\lambda = 490 \text{ nm}$ in deaerated CH_3OH (\circ) and CD_3OD (\square). Inset: second-order plots.

to the reactive intermediate iridium(II) complex (**2**)^[14] This indicates that deprotonation of **1** occurs in the excited state and that the iridium hydride complex **1** acts as an efficient photoacid. Scheme 1 summarizes the photoactivity of **1**.

The decay of the transient absorption band (Figure 1 b), which arises from the instability of **2**, obeys second-order kinetics (see inset of Figure 1 b). Thus, the following mechanism evolves: after the initial deprotonation of excited state of **1** (**1***), which generates **2** and a proton; protonation of **2** occurs in CH_3OH and regenerates the ground state **1**. This

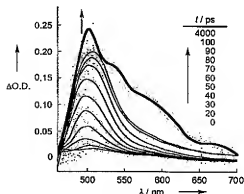


Figure 2. Transient absorption spectra observed upon formation of the ICT excited state of **1** ($1.5 \times 10^{-4} \text{ M}$; thin lines) and the following deprotonation of **1** (thick line) after laser excitation ($\lambda = 355 \text{ nm}$, 1.5 mJ/pulse) in deaerated CH_3OH .

355 nm) of **1** in deaerated CH_3OH , a new absorption band with a maximum at 500 nm increase steadily up to 100 ps . This absorption band is assignable to the ICT excited state of **1** and the underlying growth dynamics corresponds to the intersystem crossing (ISC) to form the lowest triplet excited state of **1**. In this lowest triplet excited state of **1**, the 2,2'-bipyridine (bpy) ligand is reduced to its radical anion, exhibiting the characteristic visible absorption band at $500\text{--}600 \text{ nm}$.^[16] Moreover, the absorption maximum at 500 nm is consistent with that observed for metal-to-ligand charge transfer

(MLCT) excited state of other Ir^{III} -bpy complexes (490–500 nm) containing *ortho*-metalating ligands 2-phenylpyridine or benzo[*h*]quinoline.^[17] The rise of the ICT band at 500 nm obeys to first-order kinetics (see Supporting Information). The first-order rate constant ($1.4 \times 10^{10} \text{ s}^{-1}$) is consistent with that determined for the ISC of the excited state of an Ir^{III} complex bearing a 1,10-phenanthroline ligand ($3.4 \times 10^{10} \text{ s}^{-1}$).^[18,19] With the completion of the fast ISC process, the slower deprotonation process sets in, as shown in Figure 2. Here, the characteristic absorption band that relates to **2** increases with first-order kinetics (see Supporting Information). From the first-order plot the deprotonation rate constant for **1** is determined as $k_{\text{H}} = 8.1 \times 10^6 \text{ s}^{-1}$.^[20]

Although no deprotonation of **1** is observed when a CH_3OH solution of **1** is photoirradiated in the steady state (see above), the H/D exchange of **1** clearly occurs during photoirradiation in CD_3OD . For example, when a CD_3OD solution of **1** is photoirradiated in the steady state, the ^1H NMR signal at $\delta = -10.7$ ppm due to the hydride proton of **1** disappears gradually as the photoirradiation progresses (see Figure 3a). The addition of H_2O [$\text{H}_2\text{O}/\text{CD}_3\text{OD}$ (1:4 v/v)] to the photoirradiated solution results in no change in the ^1H NMR signal (Figure 3b). However, the photoirradiation of the sample in the presence of H_2O results in the

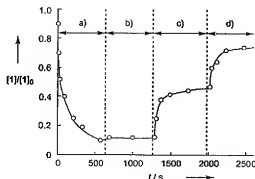
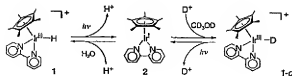


Figure 3. Plot of $[I]/[I]_0$ versus time in the photoinduced H/D exchange reaction of **1** ($8.2 \times 10^{-4} \text{ M}$) at 298 K; a) during irradiation of monochromatized visible light at $\lambda = 430 \text{ nm}$ in deaerated CD_3OD ; b) in the dark in the presence of H_2O [$\text{H}_2\text{O}/\text{CD}_3\text{OD}$ (1:4 v/v)], and during irradiation with monochromatized visible light at $\lambda = 430 \text{ nm}$ in deaerated c) $\text{H}_2\text{O}/\text{CD}_3\text{OD}$ (1:4 v/v) and d) $\text{H}_2\text{O}/\text{CD}_3\text{OD}$ (1:2 v/v).

reappearance of the hydride proton of **1** (Figure 3c).^[21] A further addition of H_2O [$\text{H}_2\text{O}/\text{CD}_3\text{OD}$ (1:2 v/v)] followed by photoirradiation of the sample results in an increase in the hydride proton signal up to 80% of **1** (Figure 3d).^[22] This observation indicates that the H/D exchange occurs efficiently during the photoirradiation of **1** in CD_3OD in the steady state as shown in Scheme 2.

The deprotonation of the excited state of **1** may be understood by comparing the case of photoacid formation of hydroxyarenes, in which the enhanced acidity in the excited state is ascribed to an ICT from the hydroxyl oxygen to the aromatic ring. Figure 4 shows the HOMO and LUMO orbitals of **1**, obtained by DFT calculations.^[23] The HOMO



Scheme 2. The H/D exchange reaction between **1** and $[\text{D}]_2\text{1}$ under steady-state photoirradiation.

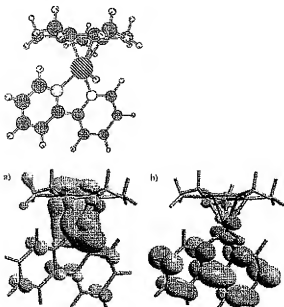


Figure 4. a) The HOMO and b) LUMO orbitals of **1** calculated based on a density functional theory using ADF 2003.01 program.^[23]

orbital is highly localized on the metal center, whereas the LUMO orbital is mainly localized on the ligand moiety. Thus, the MLCT excitation reduces the basicity of the iridium metal center, thus facilitating the release of a proton from **1**. The lifetime of the excited state of the conjugate base **2** is too short to be detected in the transient absorption spectra in Figure 2. On the other hand, the oxygen-centered hydroxyarenes have fluorescent conjugate bases with nonbonding molecular orbitals and excited states with charge distribution at distant sites from the oxygen atom. This reduces the basicity of the conjugate base. The latter scenario is equivalent to Weller's "intramolecular charge transfer" rationalization of the enhanced acidity in photoexcited hydroxyarenes.^[2] The iridium hydride complex **1** also has a conjugate base **2** in which the MLCT transition reduces the basicity of the iridium metal center, thus facilitating the release of protons from the excited state of **1**.^[24,25]

In summary, the present study documents a detailed investigation regarding 1) photoinduced deprotonation and 2) H/D exchange processes in a metal hydride complex **1**. We believe that **1** represents a new class of unique candidates that exhibit promising features as visible light-sensitive PAG.

Experimental Section

The iridium hydride complex, **1**, was synthesized according to the literature procedure.^[9] The methanol solution of deuterium-exchanged complex **1** ($[D_4]-1$) for picosecond laser flash photolysis experiments is obtained by the photoirradiation of **1** in the steady-state for 20 min by continuous exposure to light from a Xe-lamp (150 W, $\lambda > 390$ nm) in deaerated $[D_4]$ methanol (CH_3OD).

Laser flash photolysis: For nanosecond laser flash photolysis experiments, the deaerated methanol solution of **1** was excited by a Panther OPO pumped by Nd:YAG laser (Continuum, SLI-10, 4–6 ns fwhm) at $\lambda = 430$ nm with the power of 10 mJ per pulse. The photochemical reactions were monitored by continuous exposure to a Xe-lamp (150 W) as a probe light and a photomultiplier tube (Hamamatsu 2949) as a detector. Picosecond laser flash photolysis experiments were carried out with 355 nm laser pulses from a mode-locked, Q-switched Quantal YG-501 DP Nd:YAG laser system (pulse width ~18 ps, 1–3 mJ/pulse).^[10] The white continuum picosecond probe pulse was generated by passing the fundamental output through a D_2O/H_2O solution.

Theoretical calculation: Electrons in orbitals up to and including **1s** (**CN**) and **4f** excluding **5s** and **5p** (**Ir**) were treated in accordance with the frozen-core approximation. Calculations for **1** and **2** were spin-restricted. Geometry optimizations were performed by using the local density approximation (LDA) with double- ζ quality Slater type basis sets (type II) for C, H, and N atoms and triple- ζ (type IV) for Ir atom. Nonlocal and relativistic corrections to the LDA were effected employing the B-LYP nonlocal exchange and correlation functionals and the ZORA scalar relativistic correction for each atom.^[11]

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- [20] The kinetic deuterium isotope effect (k_H/k_D) on the rate of deprotonation of **1*** is significantly smaller than that observed in the protonation process of **2**.
- [21] The reappearance of the hydride proton signal by the addition of H_2O (part c, Figure 3) clearly indicates the formation of the Ir-D complex, although we have not confirmed its formation by 1H NMR.
- [22] Addition of H_2O obviously accelerates the rate of H/D exchange. It takes more than 600 seconds for reaching H/D exchange equilibrium of **1** (Figure 3a), however, less than 300 seconds in the presence of H_2O (Figure 3c and d).
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